

KOHOUT

The Determination of Ash as Affected by
Certain Mineral Constituents of Coal

Chemistry

B. S.

1913

THE UNIVERSITY
OF ILLINOIS
LIBRARY

1913
K82



THE DETERMINATION OF ASH AS AFFECTED BY
CERTAIN MINERAL CONSTITUENTS OF COAL

BY

JEROME FRANCIS KOHOUT

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

1913

1913
K82

UNIVERSITY OF ILLINOIS

May 28

1913.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Jerome Francis Kohout

ENTITLED The Determination of Ash as Affected by Certain

Mineral Constituents of Coal.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry.

E. C. Van

Instructor in Charge

APPROVED:

W. A. Noyes

HEAD OF DEPARTMENT OF

Chemistry

247406

Table of Contents.

Introduction	page 1.
I. Calcium Carbonate	4.
II. Methods for Determining Ash	10.
III. Ferrous Sulphate	14.
IV. Iron Pyrites	21.
V. Ash Determined in Crucibles	22.
VI. Addition of Calcium Carbonate	23.
VII. Addition of Iron Pyrites	25.
VIII. Addition of Sulphuric Acid	26.
IX. Qualitative Analysis of Ash	27.
X. Ash Determined in Milk Dishes	28.
XI. Quantitative Analysis of Ash	30.
Conclusions	42.



Digitized by the Internet Archive
in 2013

<http://archive.org/details/determinationofa00koho>



List of Tables.

Table No. 1. Growth of Sulphate in Finely Ground Coal.	page 15.
2. Carbon dioxide in Coals	17.
3. Influence of Fine Grinding on the Increase of Sulphate in Coal.	18.
4. Dilute HCl and Dilute Na_2CO_3 as Extracting Agents.	20.
5. Comparison of Actual and Calculated Ash Values	21.
6. Ash with Iron Pyrites Added.	22.
7.	22.
8. Analysis of Ash, Referred to Original Coal.	23.
9. Calculation of Sulphate to FeSO_4 from SO ₃ and Fe Determinations.	34
10. Comparison of Ash in Coal 4993.	37.
11. Distribution of Sulphate in Coal 4993.	37.
12. Comparison of Ash Values in Coal No. 5123.	39.
13. Distribution of Sulphate in Coal 5123.	39.
14. Disposition of Sulphate.	40.
15. Effects of Rate of Combustion.	42.

The Determination of Ash as Affected by Certain Mineral Constituents of Coal.

Introduction.

The constituents of coal may be divided into two general classes, the organic or combustible, and the inorganic or noncombustible material. Any study of coals for inspection of such material for technical or industrial purposes involves the determination of each of these two types of substance.

In the form of a chart, for example, we might represent the facts thus stated, as follows :-

Coal	(	Organic or	
		(	
		(hydrocarbon	
	(	combustible compounds.	
	(		(Water
	(		(
	(		(Clay or Shale
	(		(
	(	Inorganic or	(Water of hydration
	(	incombustible	(Iron pyrites as FeS_2
	(	compounds	(Calcium Carbonate
			(Ferrous or Ferric Sulphate.

If we examine the cross-section of a coal seam we may see directly the distribution of some of these constituents as in Fig. 1.

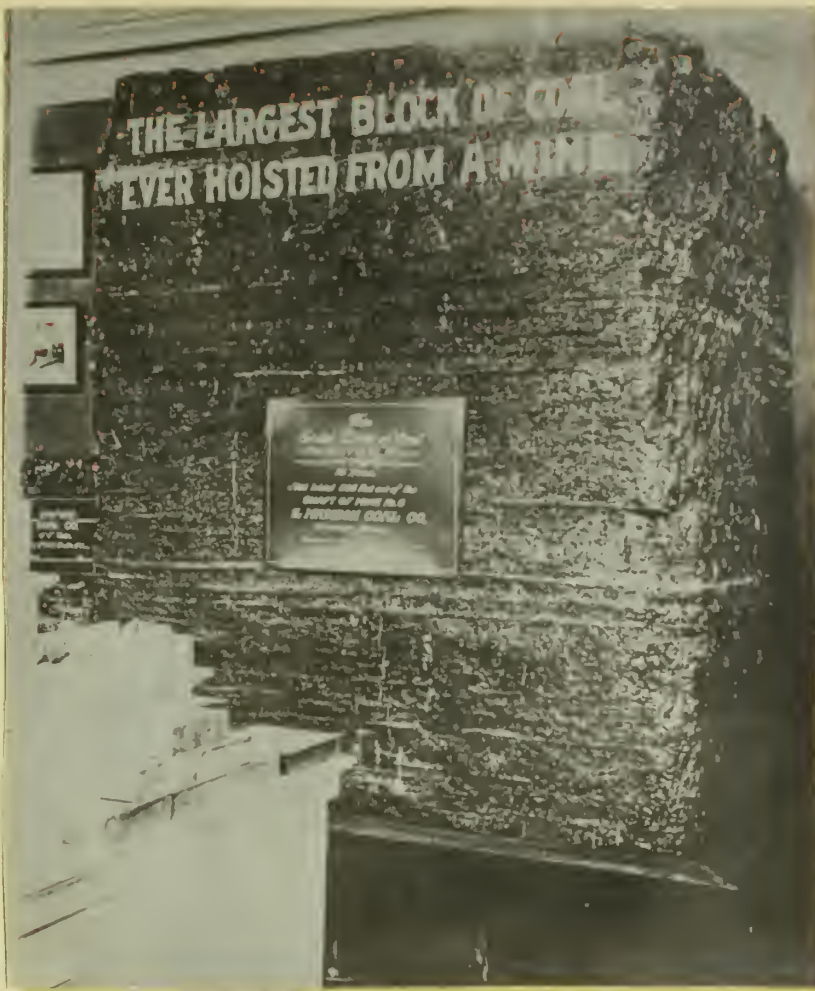


Fig. 1.

This represents a section of a coal seam. On the line of the lower edge of the placard is seen a band of pyrites. Just below this band are two more of clay and shale. At the middle of the section on a line with the words, " Shaft of Mine No. 6 "; is seen a band of clay and shale. A band is found also above the placard. The white streaks near the lower edge of the lump of coal and the white specks on it are calcite.

In determining the two divisions as above shown, the natural method would be to burn off the organic or combustible portion with the idea that the inorganic or noncombustible

substance would remain. This in general would be true but certain sources of error or difficulty arise. The inorganic moisture we may dismiss as presenting no difficulty as it is easily removed and our basis for determination may well be considered as the " oven dry " or moisture free form.

The sources of difficulty are therefore as follows:-

- (a) The presence of calcium carbonate
- (b) The presence of sulphates
- (c) The presence of pyritic iron in association with calcium carbonate.

These substances present difficulties for the following reasons :-

(1) Calcium carbonate begins rapid decomposition into CaO and CO_2 at and above nine-hundred degrees C, below that temperature decomposition is partial but evident at temperatures above six-hundred degrees or a dull red, and must be considered.

(2) Calcium oxide in the presence of iron pyrites readily takes up sulphur and retains the same in the form of calcium sulphate. Attention should be called in this connection also to the fact that where calcium oxide is present the sulphur from the gas flame may be readily absorbed with the formation of calcium sulphate.

(3) If high temperatures are maintained during the process of burning off the carbon the quantity of sulphate is seriously modified by reduction in the presence of red hot carbon.

(4) Temperatures which are carried to the fusion point will further modify normal constituents by the formation of calcium silicate and the liberation of sulphur trioxide.

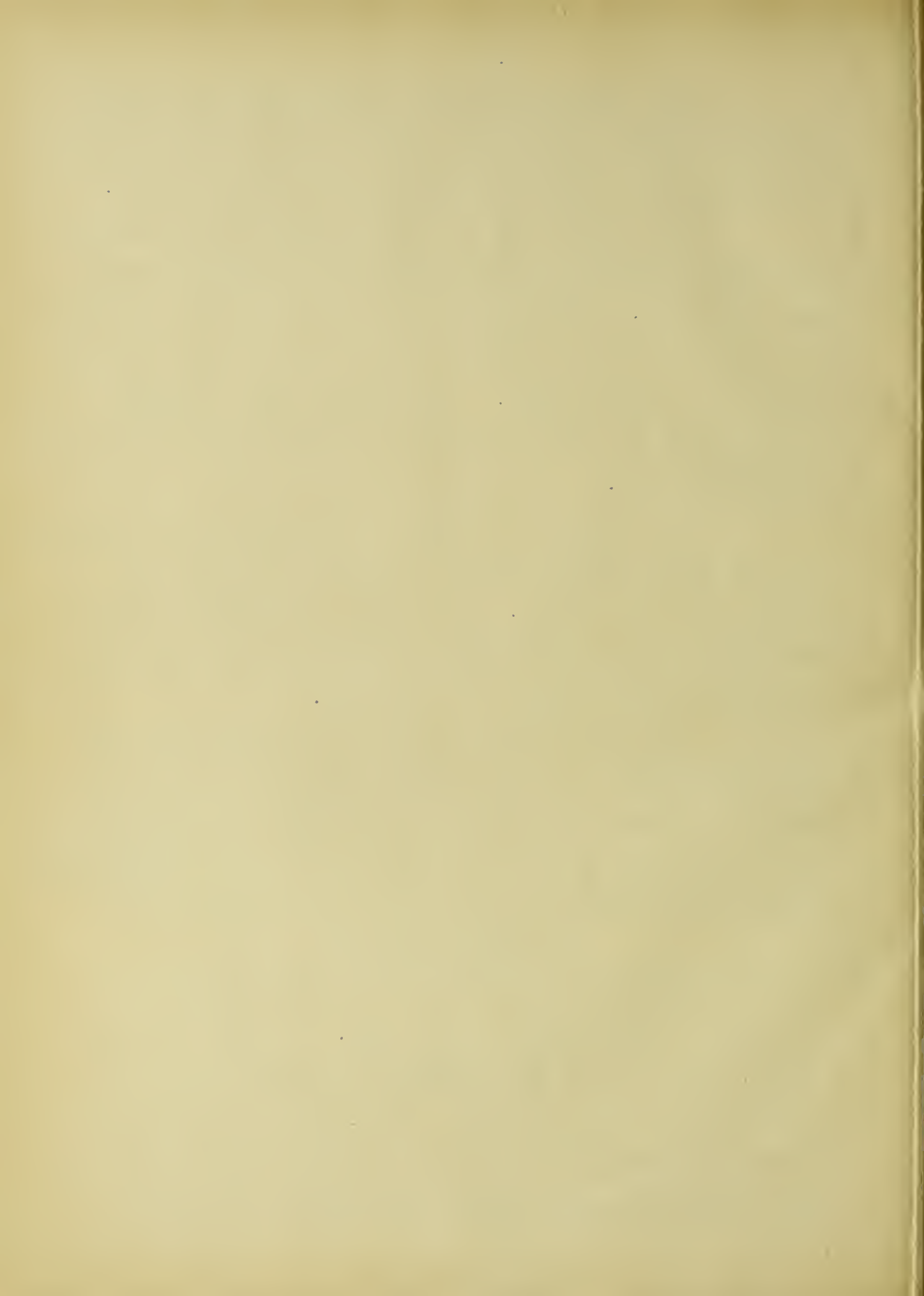
(5) Ferrous sulphate is decomposed at five hundred and fifty to six hundred degrees and ferric sulphate at seven hundred degrees. With the temperature necessary for burning off the carbon there is likely to be a transfer of sulphur trioxide to the calcium oxide. The decomposition of calcium sulphate does not occur below eleven hundred degrees in the absence of carbon.

(6) Sulphur in the form of iron pyrites is completely oxidized at the low temperatures indicated along with the burning out of the carbon. If it is so discharged it does not operate to disturb the values by uniting with calcite, but in so far as CaO develops, it is retained.

In view of these facts which are simply assembled from accepted data of common knowledge the question naturally arises as to how widely distributed are these disturbing elements, and are the quantities met with sufficient in amount to seriously affect the ash determinations as ordinarily carried out ?

I. Calcium Carbonate.

Calcium carbonate is a constituent of practically all coals at least of the Illinois type. In 1909 Prof. Parr and Mr. Wheeler (1) found it present in coal in amounts from traces to almost five per cent. Prof. Parr (2) found that in an examination of two hundred and thirty-five coals two of them had a content of carbon dioxide exceeding four per cent or



representing calcium carbonate over ten per cent of the weight of the coal. Also, five examples exceeded two per cent of carbon dioxide representing an amount of calcium carbonate in excess of five per cent of the total weight. There were also thirty-six samples with more than one and less than two per cent of CO_2 , or over fifteen per cent of the two hundred and thirty-five samples had an amount of carbon dioxide in excess of one per cent. In addition, if all samples were counted which had a sufficiently high content of this substance to represent a content of calcite in excess of two per cent, the number would reach fifty-five in two hundred and thirty-five samples, or over twenty three per cent.

Continuing this work Prof. Parr (5) obtained results on over three hundred and fifty two samples of coal from over one hundred mines in the state. The data collected shows that thirty coals or about nine per cent have carbon dioxide present in an amount less than one tenth of one per cent or less than two tenths of one per cent of calcium carbonate the form in which the carbon dioxide occurs. About fifty per cent of the samples have calcium carbonate present in excess of one per cent of the raw coal, twenty per cent have more than two per cent, and three per cent of the samples have more than four per cent of calcium carbonate, with a few isolated cases reaching as high as ten per cent of calcium carbonate in the raw coal.

In the course of the present work, in an examination of seventeen samples, five, or over twenty nine per cent had less than one per cent calcium carbonate. Three samples, or

more than seventeen per cent, had more than one per cent and less than two per cent calcium carbonate. Six samples, or over thirty-five per cent, had more than two per cent and less than three per cent calcium carbonate. Two samples, or about twelve per cent, had more than three per cent and less than four per cent of this substance. One sample, or about six per cent, had more than four per cent of calcium carbonate.

All these results indicate that calcium carbonate is likely to be met with in considerable amounts in coal.

The data with reference to the amount and distribution of sulphate in the coal is more limited than in the case of carbonate. Prof. Parr and Mr. Kressmann (4) in their work on the spontaneous combustion of coal, found water soluble sulphur, or sulphate, present in the raw coal to the amount of about two-hundredths of one per cent "water soluble sulphur" or forty-seven thousandths of one per cent sulphur trioxide.

In the present investigation, out of a total of twenty-two samples examined, sulphate was found in twenty-one of them or in ninety-five per cent of the total number. Fourteen of the samples, or about sixty-three per cent had sulphur trioxide in amounts ranging from thirteen one hundredths of one per cent to forty-seven hundredths of one per cent. Six of the samples, or over twenty-seven per cent had sulphate present from fifty-one one hundredths of one per cent to ninety-five one hundredths of one per cent sulphur trioxide. One sample, or five per cent, had sulphate in it to the amount of one and forty-two hundredths per cent sulphur trioxide.

These results are surprising, and from the data available, seem to indicate that sulphates are about as common in occurrence as carbonates.

The largest part of the sulphur of Illinois coals occurs as iron pyrites, FeS_2 . Prof. Parr and Mr. Kressemann (7) state that coals of the Illinois or mid-continental field have a content of about six per cent of iron pyrites or about three per cent of sulphur. The same facts will be noticed by an examination of the records of the fuel laboratory of the Illinois State Geological Survey located at Urbana, Ill. From these records it appears that the sulphur of Illinois coals runs up as high as four and one half per cent or up to about eight per cent of iron pyrite.

Calcium carbonate is, of the mineral constituents of coal under consideration, the one heretofore most tested for. The carbonate content of the coal is determined by liberating the carbon dioxide with acid and measuring it volumetrically. The apparatus used is a modification of that described for the determination of total carbon in coal, soils etc. (6)

In this apparatus the carbon dioxide liberated is absorbed in a large pipette containing caustic potash solution, and the residual gas is returned to the burette for measuring. The contraction in volume thus measures the amount of carbon dioxide present, and this volume is converted into gravimetric terms by reference to a table devised by Prof. Parr for this purpose. (7) The carbon dioxide thus determined is then calculated to calcium carbonate. This constitutes the quickest

and most commonly used method for the determination of calcium carbonate in coal. This method, however, is open to a serious objection, namely that all the carbon dioxide is considered as coming from calcium carbonate. This is not always true. Very appreciable amounts of magnesium or iron carbonates may be present, and if so, to calculate all the carbon dioxide to calcium carbonate would introduce a considerable error.

To check the results for calcium carbonate as obtained by the carbon dioxide determination described above, it is best to determine the amount of calcium present. This value for calcium is then calculated to calcium carbonate, and if the two results check each other, the carbon dioxide may be considered as coming from the calcium carbonate in the coal. The determination is best made volumetrically, though a gravimetric method may be used. A definite quantity, about five grams, of coal is weighed out, placed in a suitable flask or beaker, and boiled with about one hundred cubic centimeters of ten per cent hydrochloric acid. In place of this, the contents of the flask from the carbon dioxide determination may be used. After all the carbonate is decomposed, the coal is filtered off and the filtrate is heated to boiling. A few drops of concentrated nitric acid are added to oxidize any ferrous iron to the ferric state and the iron and aluminum are precipitated from the hot solution with ammonium hydroxide. The precipitated hydroxides are redissolved in hydrochloric acid and reprecipitated with ammonia. The filtrate from the second precipitation is added to that from the first and the lime is determined in the

combined filtrates. The reason for the second precipitation of iron and aluminum is because of the fact that the first precipitate usually carries some lime down with it, which would thus be lost in the calcium determination.

The combined filtrates are heated to boiling, ammonia water is added if the liquid is not distinctly alkaline, and the calcium is precipitated from the hot solution with sixteen cubic centimeters of a boiling saturated solution of ammonium oxalate. The contents of the beaker are kept at the boiling point for five minutes to settle the calcium oxalate. The beaker is allowed to cool and the precipitated calcium oxalate is filtered off, and washed several times with hot water, rinsing out the beaker onto the filter paper the first few times. The filter paper is then spread against the side of the beaker in which the precipitation took place, and the precipitate is washed off the paper into the beaker with hot water; the last two washings being made with ten per cent sulphuric acid. Fifty cubic centimeters of water and ten cubic centimeters of concentrated sulphuric acid are then added to dissolve the precipitate. When it is all in solution, the solution is boiled, and titrated while hot with a standard potassium permanganate solution. This is the method suggested by W. L. G. for the determination of lime in Portland cement and in the red cement is used in cement investigations. (c) To determine the lime gravimetrically the lime cement is the same as in the volumetric method up to the point where the precipitate of calcium oxalate is washed from the filter paper.

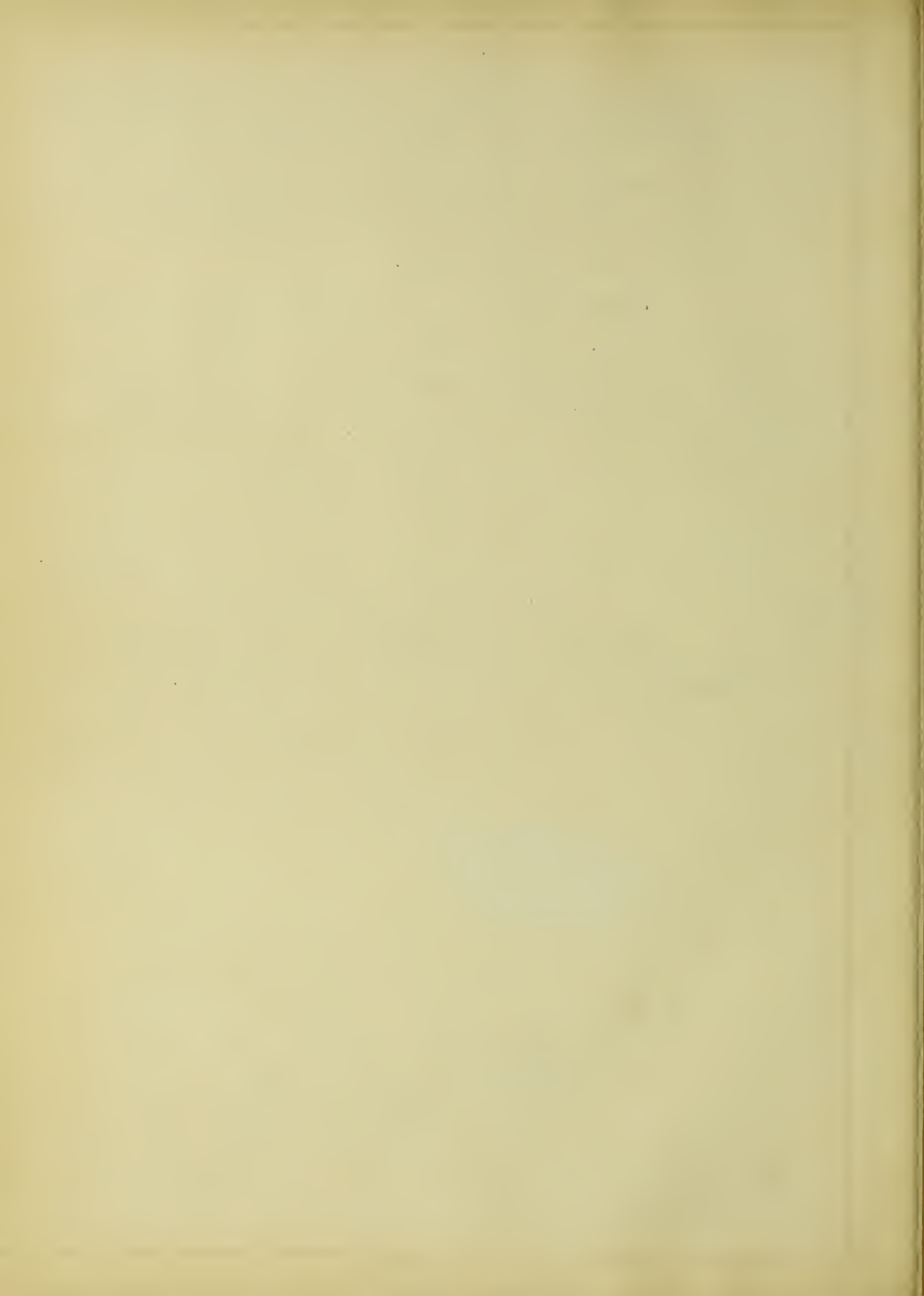
Instead of dissolving the calcium oxalate, the precipitate and filter paper are burned in a weighed platinum crucible and ignited to a constant weight by means of a blast lamp. The calcium oxalate is decomposed by the heat and the precipitate is weighed directly as calcium oxide.

CaCO_3 decomposes at nine hundred degrees and the CO_2 is eliminated. If this CO_2 is not accounted for in the ash an error is made in that value and also in the value of other constituents arrived at by difference. In the ultimate analysis the factor for total carbon is affected if the carbon dioxide resulting from the decomposition of the CaCO_3 is not subtracted from the total CO_2 as determined in the total carbon apparatus.

II.-Methods for determining ash.

The report of the Committee on Coal Analysis (9) includes the following method for ash determination. The portion of powdered coal from the moisture determination is burned, at first with a very low flame, with the crucible open and inclined, until free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter. It is advisable to examine the ash for unburned carbon by moistening it with alcohol.

When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of ash, and, since three atoms of oxygen replace four atoms of sulphur, the weight of the ash is less than the weight of the mineral matter in the coal by five eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee does not



recommend such a correction for "proximate" analysis. When analyses are to be used as a basis for calculating the heating effect of the coal a correction should be made.

This correction is shown in the calculation of the calorific value according to Dulong's formula, which gives the calorific power in calories per kilogram.

$$\text{Calorific power} = 8080 C + 34,460(H - 1/80) + 3230 S.$$

In the laboratory of the Ohio State Geological Survey (10) the moisture in coal is determined in special porcelain capsules which are then used for the ash determination, without further transferring of the contents. The sample is burned to ash in a muffle, care being taken to begin the burning off at a low heat to avoid coking of the coal, the temperature of the muffle being raised to redness after the expulsion of the volatile matter. Heating is continued till all black carbon is burned out, the capsule is then removed from the muffle furnace and allowed to cool in the open air and weighed as soon as cooled, it is then replaced in the red hot muffle for from fifteen to thirty minutes, again allowed to cool and reweighed, continuing this process if necessary till constant weight is obtained.

In the laboratory of the Illinois State Geological Survey the contents of the glass capsules are transferred to a small porcelain crucibles for the ash determination. The dry coal in the crucible is heated at a very low temperature just sufficient to ignite the coal and to keep it burning. After the carbonaceous matter has all burned out, the crucible

is blasted for fifteen minutes to drive off the carbon dioxide of the carbonate present in the coal. This ash is then corrected by adding the carbon dioxide to it and also eight per cent of its weight as a hydration factor to account for the water in the clay and shale constituents of the ash.

The following method of ash determination is used by engineering students taking the course in gas and fuel analysis at the University of Illinois. (11) One gram of the dry coal is weighed in a weighed porcelain crucible, which is then placed two or three inches above the extreme tip of a flame turned down to about two inches in height. It is left in this condition for fifteen or twenty minutes, by the end of which time most of the carbonaceous matter has been burned out. It is then lowered to within one half or one quarter inch of the flame and left without attention for an equal length of time. Occasional stirring with a platinum wire will facilitate the oxidation. The crucible is finally placed in an inclined position to facilitate the circulation of air, and a flame from a blast lamp is applied from five to ten minutes or to constant weight. The crucible is then cooled in a desiccator and weighed.

Franz Weisser (12) found that the ash content of coals varies both in per cent and composition according to the method, duration and temperature used. A high temperature decomposes the carbonate or replaces it with SO_3 . If the ignition is prolonged the SO_3 content of the ash grows. When the coal is ashed in a muffle or stream of oxygen the ignition is complete in fifteen minutes and the results are constant, further ignition not only does not change the percentage of ash but the ash is free

from residual carbon dioxide and the percentage of sulphur trioxide remains constant. As a result of these changes taking place in the mineral constituents of coal during ignition, it is evident that the results obtained in a muffle are too low because of the loss of carbon dioxide while the results with a free flame are nearer the truth, but the ash is variable both as to total percentage and composition. Weissers suggests the following scheme for determining the ash in coal.

True ash = ash in muffle - total Fe_2O_3 - SO_3 in ash + sulphate, SO_3 , and CO_2 in raw coal + FeS_2 + soluble FeO in raw coal. The determination of FeS_2 is based on its insolubility in dilute H_2SO_4 . Therefore FeS_2 = Total Fe in ash - Fe soluble in dilute H_2SO_4 in coal.

Prof. Parr and Mr. Wheeler (13) carried the ash to the point of fusion in a platinum crucible. By this method all the carbon dioxide was driven off along with the chlorine which might be present in the coal. They correct the ash by adding these two factors to it. In the case of sulphur trioxide present in the coal as ferrous sulphate, they consider that this constituent does not need to be corrected for since it would be eliminated during the ashing process.

The above outlined methods are all at fault at least as they do not take account of the sulphate in the raw coal. This constituent does remain behind in the ash, being retained by the basic matter present. Calcium oxide will also take up sulphur from a gas blast lamp flame so those methods which use such a scheme are in error in that also. When the ash is

carried to the fusion point to be certain of eliminating the carbon dioxide by the reaction of calcium carbonate with silicious matter to form calcium silicate some of the calcium sulphate present may also react with the silica and thus drive out the sulphur trioxide from the ash. This would cause an error in the ash determination.

The calcium oxide present in the coal ash will react with the sulphur trioxide resulting from the decomposition of the coal ash so it is of importance to consider this substance as a constituent of coal ash.

The following are suggested as being required for a proper determination of ash in coal.

(a) A muffle with a good circulation of air, and a temperature from seven hundred to seven hundred and fifty degrees centigrade.

(b) A determination of the carbon dioxide in the raw coal and the addition of this factor to the ash.

(c) In the absence of sufficient basic matter to combine with the sulphate present in the raw coal as shown by the low carbon dioxide factor, add about five per cent of dry calcium carbonate to the coal before ashing, and subtract the equivalent of calcium oxide resulting from the decomposition of the calcium carbonate added.

How these suggestions are to be applied will be shown later under an account of experimental work.

III:- Ferrous sulphate.

Ferrous sulphate is a constituent of coal the importance of which seemingly has heretofore been overlooked. It

has been found present in practically all the coals examined in the present work in amounts too great to be disregarded.

Ferrous sulphate is formed in coal by the oxidation of iron pyrites. The reaction goes according to the following equation.

$2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2\text{O} = 2 \text{FeSO}_4 + 2 \text{H}_2\text{SO}_4 + \text{heat}$. The oxidation goes further and the final product is probably a mixture of ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, and basic ferric sulphate $\text{Fe}(\text{OH})\text{SO}_4$. Also the free sulphuric acid formed may combine with some of the basic carbonates present and form sulphates.

The sulphate content of coal increases on standing. This is especially noticeable in the case of laboratory samples which are kept in storage sometimes for more than a year. These samples are ground to pass a sixty mesh sieve and are kept in glass bottles closed with rubber stoppers. A series of seven coals was analyzed at intervals for sulphate and table number one shows how the sulphate increased in the course of time.

Table No. 1.

Growth of Sulphate in Finely Ground Coal.

Lab. No.	Source County	SO ₃ 60 mesh coal		SO ₃ in buckwheat size coal.	Total sulphur
		Feb. 1913	Apr. 1913		
5365	Mercer	.95	1.46	.86	5.25
5367	Grundy	.39	.38	.12	2.87
5370	Mercer	.47	.49	.25	4.90
5372	Mercer	.63	1.25	1.12	5.46
5376	Grundy	.61	1.12	.86	2.73
5388	LaSalle	1.43	1.79	.82	5.20
5391	LaSalle	.62	1.20	.81	4.23

Results all given on moisture free or dry basis.

The determinations made in February, 1913 were on washings from the flask of the carbon dioxide apparatus and had been standing in a ten per cent solution of hydrochloric acid in covered glass beakers from August 1912. The determinations made in April, 1913 were on the laboratory samples of finely ground coal which had been in storage from August, 1912. The determinations of sulphate in the buckwheat size coal were also made in April, 1913 on coal which had been ground to buckwheat size in August, 1912 and had been in storage in quart size " Seal Fast " fruit jars from that date.

Looking at the table it is seen that all the samples except two, Nos. 5367 and 5370 increased remarkably in their content of sulphate. The two exceptions however increased their sulphate by about one hundred per cent over that in the buckwheat size sample. Sample No. 5372 which had a sulphate factor of 1.12% in the buckwheat size coal as against .63% in the finely ground sample analyzed in February, 1913 had a very large proportion of its mass in a very fine state of subdivision.

The carbon dioxide in these coals was also redetermined in April, 1913 to see if the amount of calcium carbonate originally present had decreased. Table No. 2 gives the results obtained on six of the coals

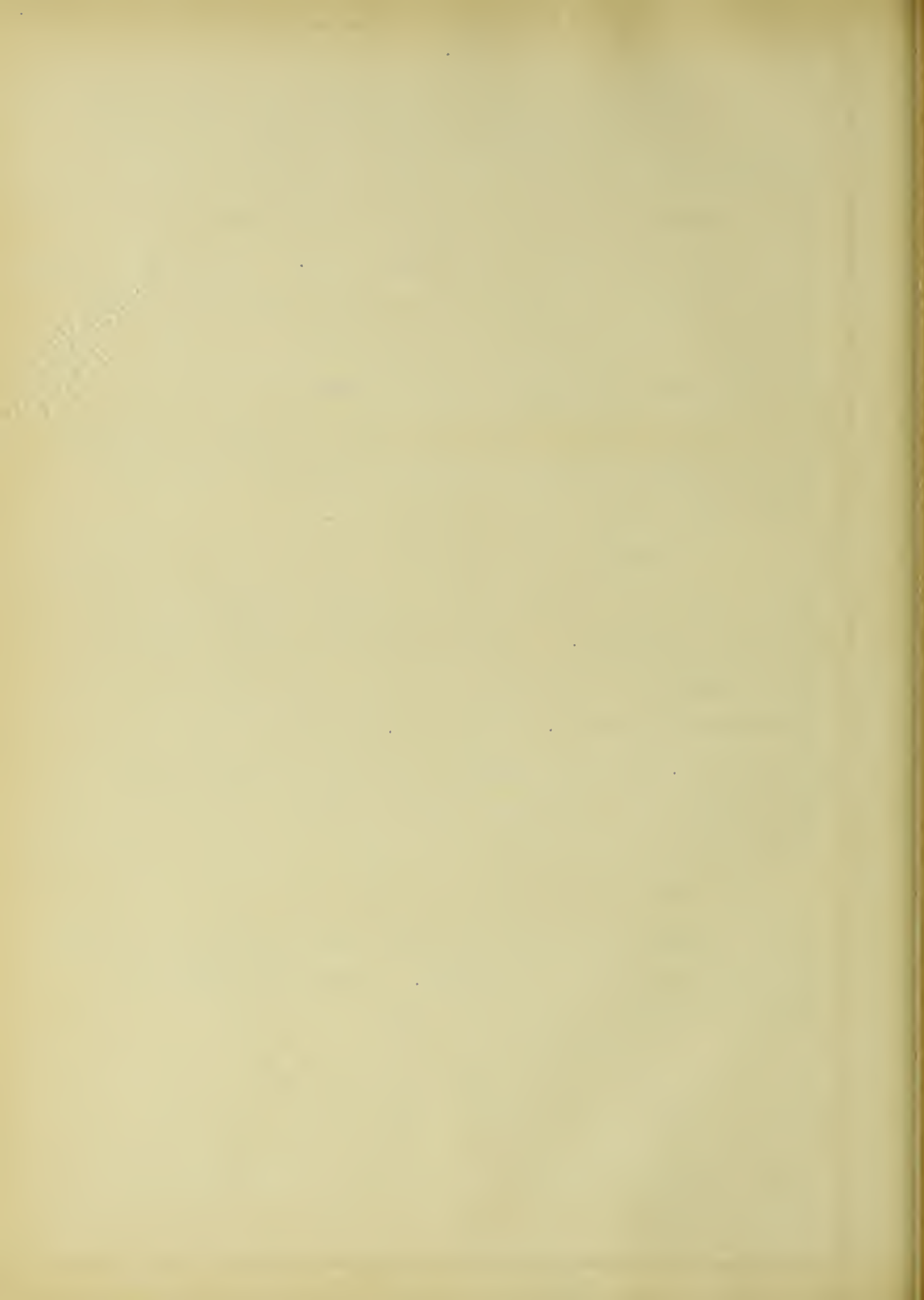


Table No. 2.
Carbon Dioxide in Coals

Lab. No.	Carbon dioxide	
	Aug. 1912	April 1913.
5365	.91%	.90%
5367	.79	.20
5370	1.15	1.14
5376	.23	.30
5388	.93	.92
5391	.34	.35

There was no change in the carbon dioxide factor in the coal. This indicates that the sulphate formed was in the form of ferrous sulphate and that no reaction took place between the calcium carbonate and whatever free sulphuric acid may have been present in the coal. This would be indicated by a decrease in the amount of carbon dioxide in the coal.

Fine grinding also has a tendency to increase the amount of ferrous sulphate in the coal. This is probably due to the exposure of a larger surface to the action of the air and moisture. To determine the extent of this influence two samples of coal, Nos. 5372 and 5388, were sized to ten, twenty, and forty mesh size and each was analyzed for sulphate. Table No. 3 shows the results obtained.

Table No. 3.
Influence of Fine Grinding on the Increase of Sulphate in Coal

Lab. No.	SO ₃		
	10 mesh	20 mesh	40 mesh.
5372	.91%	.89%	1.13%
5388	.53	.60	1.42

There is practically no increase in the sulphate content of the twenty mesh above that of the ten mesh size, but there is a very marked increase in that of the forty mesh above that of the twenty mesh size. This would indicate that possibly coal of a fineness not greater than twenty mesh may be stirred without any change in the sulphate factor taking place, but that in samples ground finer than twenty mesh the increase in sulphate in the coal is considerable.

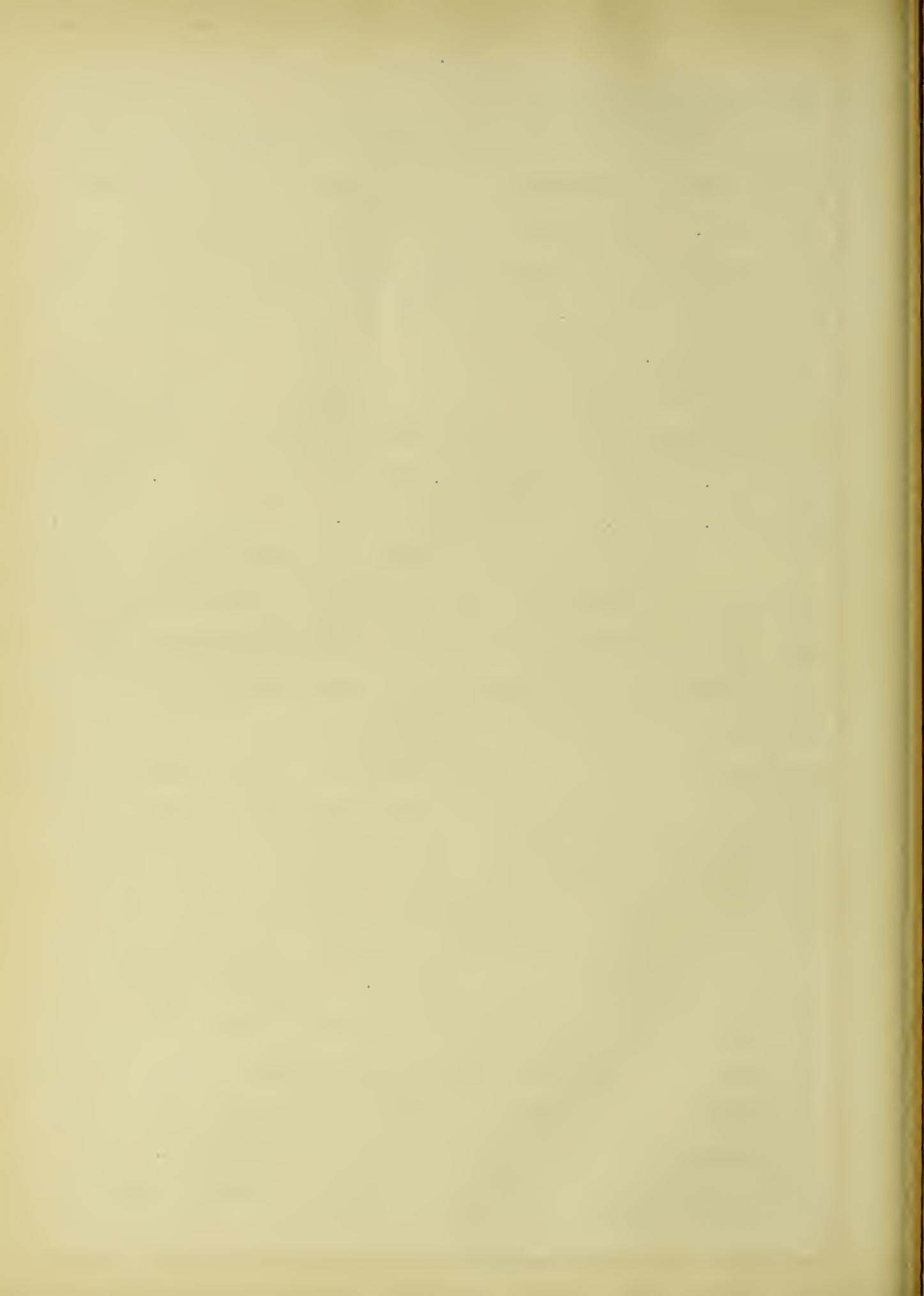
All methods for the determination of sulphate in coal depend on the extraction process. Prof. Parr and Mr. Kressmann (14) tried several methods. One was by digesting the coal with water acidified either with hydrochloric or sulphuric acid in amounts from traces to two per cent acid. Another method which they used was to leach the coal with pure boiled water. About twenty-five grams of finely ground coal were placed in a large folded filter paper and about six hundred cubic centimeters of the boiled water was poured over the sample, the latter being stirred so as to thoroughly wet the fine coal. The filtrate was then poured back over the coal, and the next filtrate, consisting of the same water first used, was again poured back over the coal, thus making three leachings with the same water. The coal was finally washed with an additional one hundred cubic centimeters of boiling water. The iron was determined in this solution also. They also tried boiling the coal with two per cent sodium carbonate solution to convert any calcium sulphate to sodium sulphate. A third method they tried was to extract the coal with ten per cent hydrochloric acid solution, since

gypsum is soluble in HCL.

Duplicate samples of twenty five grams of coal each were treated as outlined above and were put in the water bath over night. The next day they were filtered and the sulphur carefully precipitated with barium chloride after the filtrates had been concentrated. The results of the six determinations are as follows.

First Method	Second Method	Third Method
Boiling water	2% Na_2CO_3 Solution	10% HCL.
.0192% S.	.0569% S.	.0373% S.
.0187% S.	.0571% S.	.0211% S.

The third method with its large variation was discarded at once, for it seemed that the solubility of the gypsum in the acid was neither exact nor reliable. The first method gave concordant results, but compared with the second method they were much too low. After a long period of digestion the first and third methods would probably give all the calcium sulphate present but, according to the data, ten hours digestion at one hundred degrees is not sufficient. The second method gives results probably as nearly correct as can be obtained, although the solubility of calcium carbonate, which is about fifty parts in a million, would create a slight error. The sulphur obtained by the second method (as it would be from any of the three methods outlined) is, therefore, the sulphur from the ferrous and calcium sulphates. The sulphur in the ferrous sulphate, however, was determined by calculation from the water soluble iron. The difference between these two values would, therefore, give the



sulphur present as calcium sulphate.

In the present work two methods were tried in the determination of sulphate in coal and ash. The first method was the same as method number two given above. Five grams of coal were boiled for two hours with one hundred cubic centimeters of two per cent sodium carbonate solution and the coal was filtered out. The filtrate was acidified with hydrochloric acid, boiled, and the sulphate was precipitated with ten cubic centimeters of a ten per cent barium chloride solution.

In the second method five grams of coal were boiled for two hours with a one per cent solution of hydrochloric acid. The coal was filtered out and the sulphate in the filtrate was precipitated with ten per cent barium chloride solution. Table number four shows the results obtained.

Table No. 4.
Dilute HCl and Dilute Na_2CO_3 Solutions as Extracting Agents.

Lab. No.	Per cent of sulphate as SO_3 .	
	1% HCL.	2% Na_2CO_3 .
5365	1.46	1.35
5372	1.25	1.23
5388	1.79	1.60
6396	.07	.08
6406	.05	.07
6408	.12	.14
6410	.08	.10
6412	.10	.11
6414	.13	.13
6416	.07	.07
6433	.21	.22



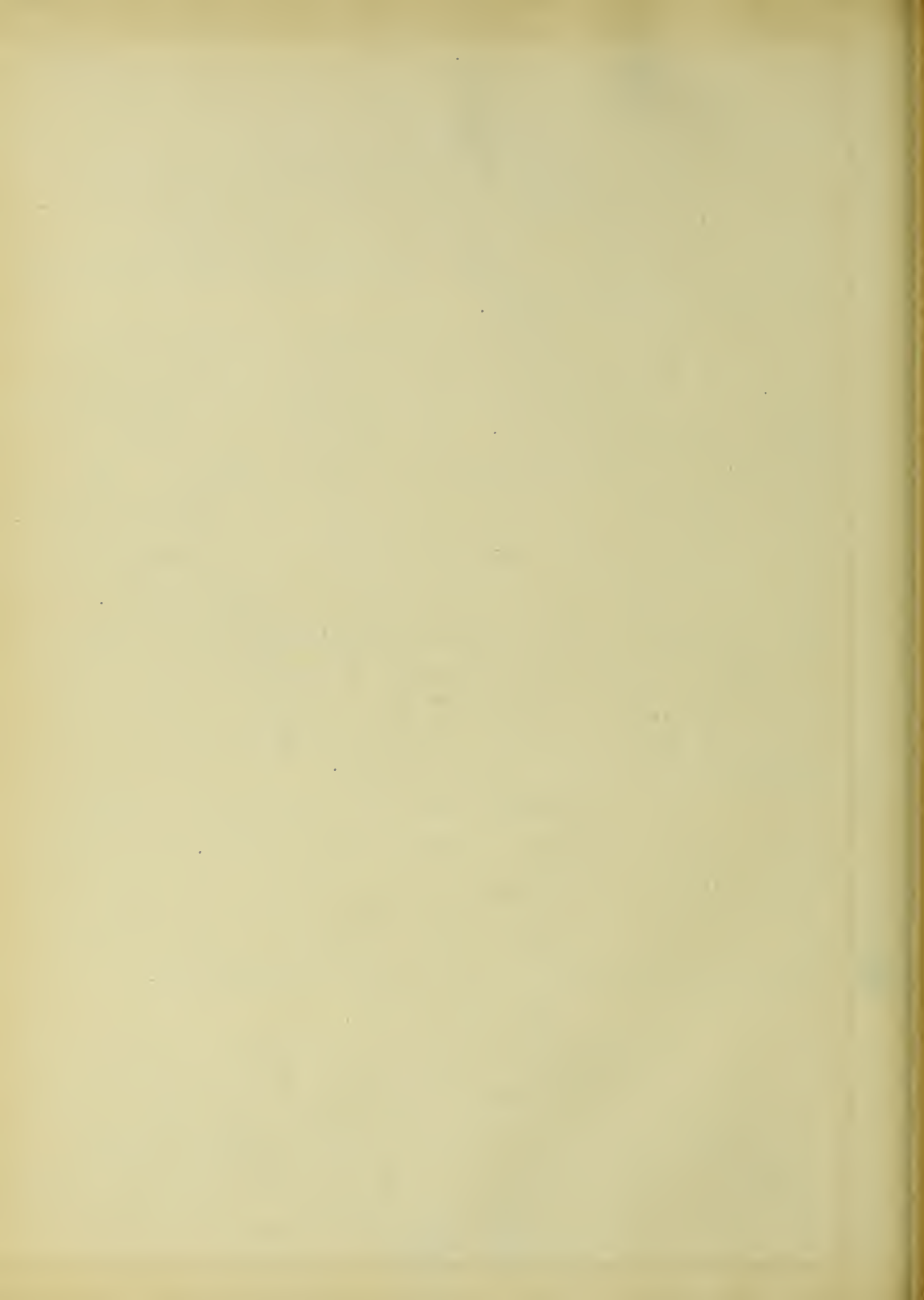
With small amounts of sulphate present there is no choice between the two solutions, but when the sulphate is present to one per cent or more the hydrochloric acid solution is the better extracting agent.

Ferrous sulphate is decomposed on heating to a red heat. (15) The products of the decomposition are Fe_2O_3 and SO_3 , or in some cases SO_2 and O . The temperature at decomposition is about five hundred degrees C. for ferrous sulphate. For ferric sulphate it is higher, being about seven hundred degrees C. If the sulphate in the coal nor in the ash is not accounted for it will introduce an error in the result for corrected ash. This is especially true in those circumstances where the ash is corrected by simply adding the CO_2 as determined on the raw coal to it plus eight per cent of the ash as weighed to correct for water of hydration of the clay or shale.

Calcium carbonate will react with sulphur trioxide to form calcium sulphate, the SO_3 replaces the CO_2 . (16) Franz Weisser (17) noticed the same thing in working with German coals. He found that if the temperature of ignition is high enough the CO_2 of the calcite is replaced by SO_3 or is driven out.

IV.- Iron Pyrites.

Iron pyrites is a constituent of almost all coals. It is the form in which most of the sulphur in the coal occurs. It is readily oxidized to ferrous and then to ferric sulphate under the combined influence of heat, moisture, and air or oxygen. Prof. Parr and Mr. Kressmann (18) found that about nineteen



per cent of the pyrite present was oxidized to water soluble iron regardless of the amount originally present in the coal.

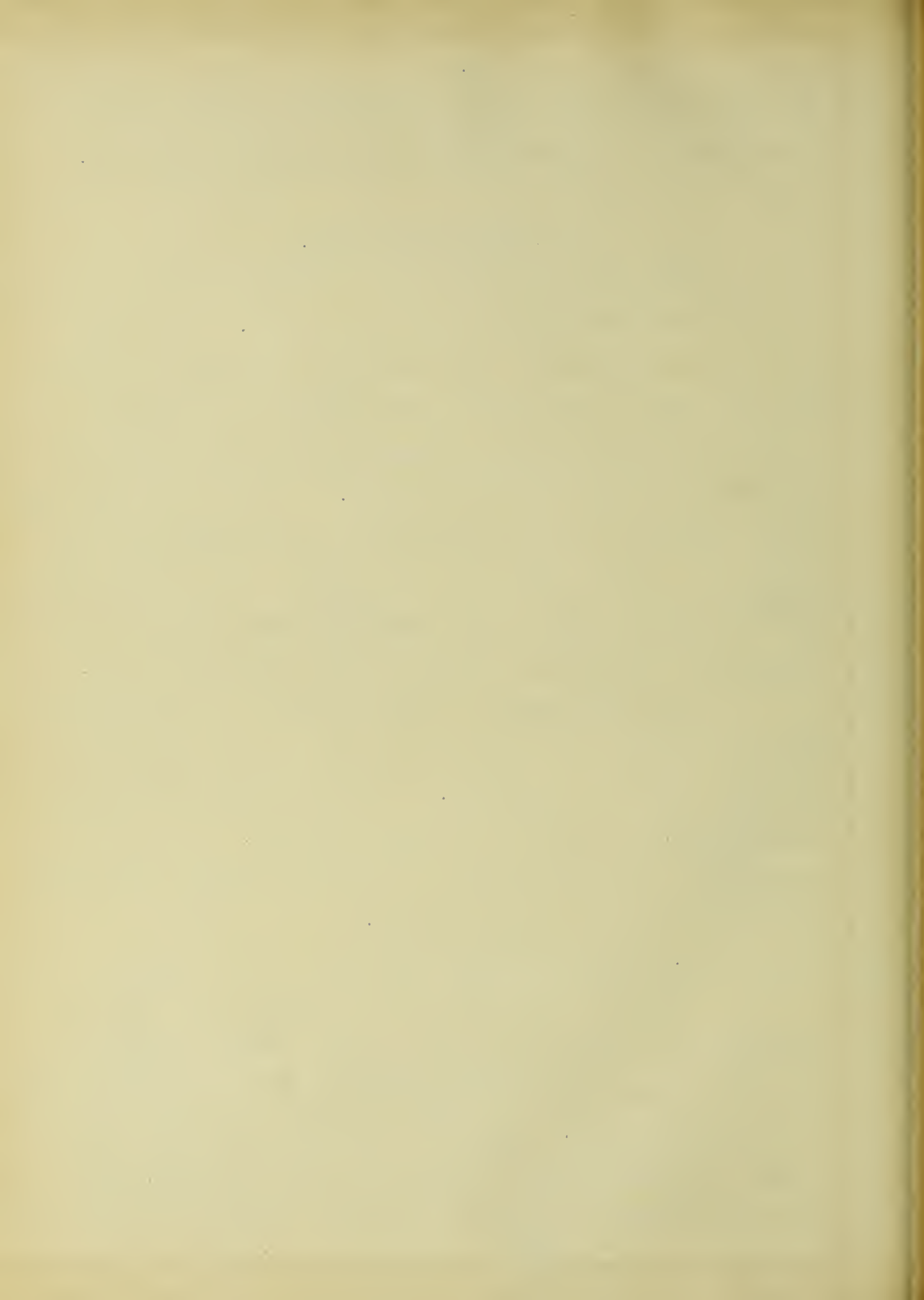
Experimental Work.

The purpose of this investigation was to work out a method for the determination of the ash in coal. To do this the effects of carbonates, such as calcium carbonate or calcite sulphides, such as iron pyrites, and sulphates like ferrous sulphate or calcium sulphate, on the noncombustible material of the coal and on each other were studied. The following questions suggest themselves; First, Do carbonates merely decompose, thus resulting in calcium oxide with loss of CO_2 ? Or, second, does the calcium oxide react in turn with the sulphur present in the coal to form sulphides or sulphates, thus increasing the ash?

In seeking answers to these questions it was thought best that for the first stages of the work, a coal should be used which contained no calcite. Thus the effect of any added calcium carbonate could be more easily followed. The coal selected for this work was known as Laboratory Sample Number 4993 and came from Saline County, Illinois.

V.- Ash determined in Crucibles.

The first undertaking was to determine the amount of noncombustible residue in the coal. This was done according to the method used in the Illinois State Geological Survey laboratory for ash determination. One gram of coal was burned in a small weighed porcelain crucible of about seven c.c. capacity. When the carbonaceous matter was all burned out, the crucible and

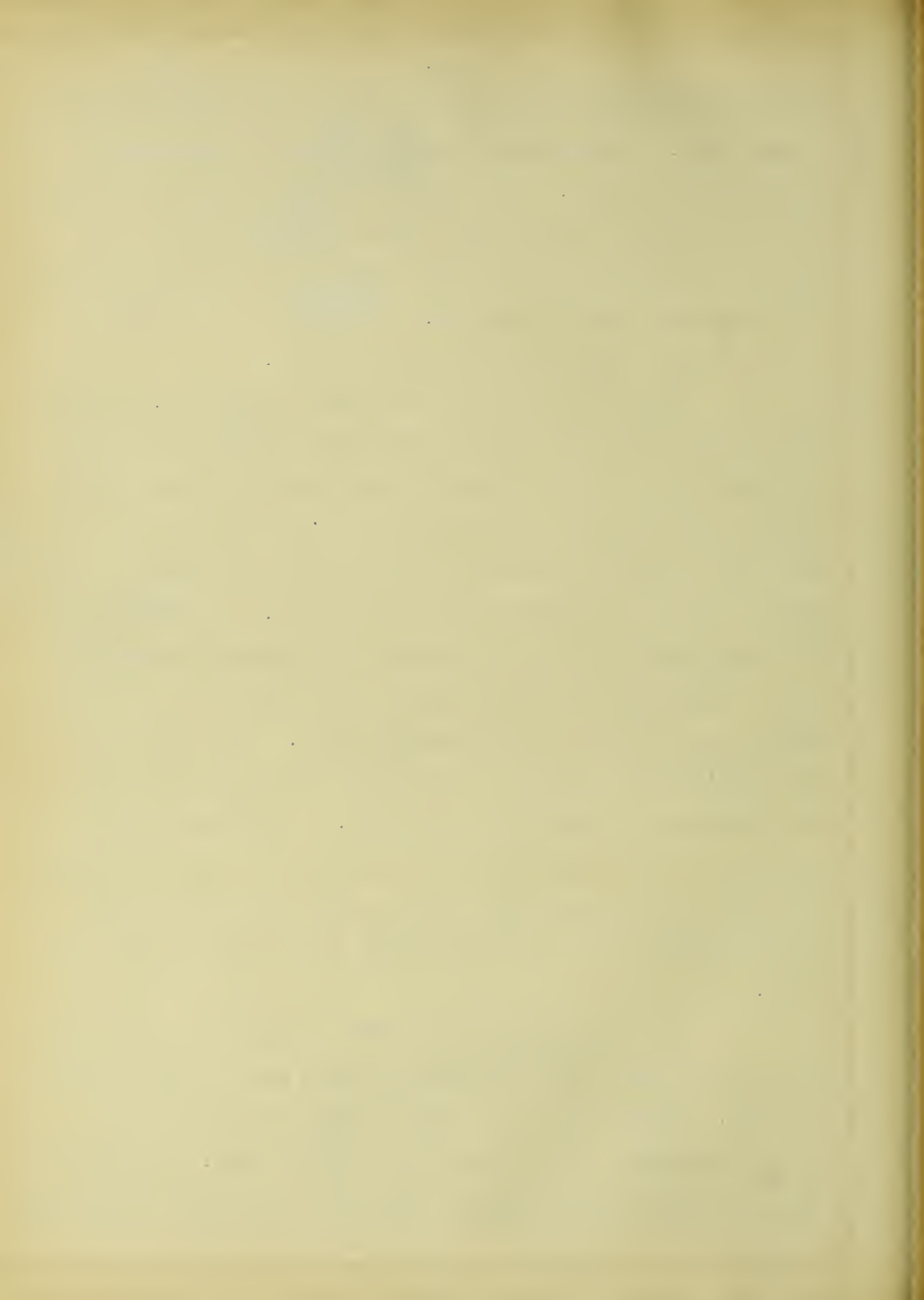


contents were ignited for fifteen minutes at the full heat of a blast lamp. The crucible was then placed in a desiccator and weighed when cool. In using this method the ash was almost invariably found to be sintered together at the bottom of the crucible, though temperatures high enough for a complete fusion of the ash could not be obtained.

VI.- Addition of Calcium Carbonate.

Calcium carbonate was now added to the coal. This was done to see whether the calcium oxide resulting from the decomposition of the calcium carbonate had an additive effect thus increasing the ash value only by so much CaO or whether it entered into combination with sulphur to form calcium sulphide or calcium sulphate which would remain behind in the ash. A series of five mixtures of coal and calcium carbonate were made up containing two per cent, four per cent, six per cent, eight per cent, and ten per cent calcium carbonate respectively. The ash of all these mixtures was carefully determined just as in the first instance when the coal alone was burned. The amount of the ash in the mixture was calculated by adding the amount of ash in the actual percentage of coal taken to the amount of calcium oxide resulting from the decomposition of the calcium carbonate added.

These calculated values were compared with the results actually obtained, but no agreement between the two sets could be found. Neither were the results found in any agreement among themselves. They followed no regular order. The following table shows the calculated results for this series of mixtures



against the results actually obtained. The discrepancies are due in part, no doubt, to the fact that the ash has a tendency to sinter on the bottom of the crucible. This effect was increased by the calcium carbonate added which fluxed the silica and iron of the ash and formed a substance which may be compared to Portland cement clinker. Also the calcium sulphate present will react with the silica and will form calcium silicates. This would cause the elimination of sulphur trioxide from the ash. Since these reactions are not quantitative they cause variable errors in the value of the ash.

Table No. 5.

Comparison of Actual and Calculated Ash Values.

Description of Sample.	Ash obtained.	Calculated Ash.
------------------------	---------------	-----------------

4993	8.09 - 8.045	
4993 2% CaCO ₃	9.52 - 9.55	9.01
4993 4% CaCO ₃	11.54 - 11.27	9.97
4993 6% CaCO ₃	12.73 - 13.12	10.95
4993 8% CaCO ₃	13.92 - 14.05	11.50
4993 10% CaCO ₃	15.95 - 16.78	12.38

The fact that the results obtained were higher than the calculated values, even though they did not check among themselves, lead to the hypothesis that the sulphur present, especially that combined with iron pyrites, combined with the free lime to form calcium sulphide. The ash was therefore tested for sulphide by placing some of it in a small casserole, adding hydrochloric acid, and covering with a filter paper wet with an alkaline solution of lead nitrate held in place with

a watch glass. This was allowed to stand for one hour. At the end of that time no blackening had occurred in the filter paper showing that no sulphides were present. (18)

VII.- Addition of Iron Pyrites.

To test the above conclusion iron pyrites was added to see if any combination took place between the sulphur and the lime, or if the effect was merely the addition of so much ferric oxide and extraneous matter to the ash of the coal. Samples were made up as follows:- eighty-eight per cent coal, ten per cent calcium carbonate and two per cent iron pyrites ; the other sample contained eighty-six per cent coal, ten per cent calcium carbonate and four per cent iron pyrites. These samples were burned in small porcelain crucibles in the usual way and were ignited for fifteen minutes on the blast lamp.

The iron pyrite was analyzed and was found to consist of 69.58% FeS_2 and 30.42% extraneous matter. The method used was to mix one tenth gram of the ground pyrite with benzoic acid, potassium chlorate, and sodium peroxide in a Parr Standard Calorimeter bomb with electric ignition. The sulphur was all oxidized to sulphur trioxide which combined with the sodium peroxide to form sodium sulphate. The fusion was dissolved in hot water, acidified with hydrochloric acid, and the sulphur was precipitated with ten cubic centimeters of ten per cent barium chloride solution. The sulphur was calculated to FeS_2 .

A theoretical value was assumed for the resulting ash which would consist of the coal ash plus the calcium combined as sulphide and the iron pyrites burned to ferric oxide, plus the extraneous material in the pyrites. The value of this

Theoretical ash was 15.60 per cent for the sample containing two per cent iron pyrites, and was 16.90 per cent for the sample containing four per cent pyrites. The table shows how the results actually obtained checked with the calculated values.

Table No. 6.

Ash with Iron Pyrites Added.

Description of sample.	Theoretical value	Result obtained
4993 10% CaCO_3 2% FeS_2	15.60%	16.07%
4993 10% CaCO_3 4% FeS_2 .	16.90%	17.71%

The fact that no hydrogen sulphide was found on analysis of the sample showed that no calcium sulphide was formed under these conditions. Since the results obtained were higher than the calculated values there must be present a compound of higher molecular weight than calcium sulphide. This may be calcium sulphate.

VIII. - Addition of Sulphuric Acid.

As a test for the possible transference of CaCO_3 to CaSO_4 a method of determining the ash by converting the calcium carbonate to calcium sulphate was then tried. For this purpose a coal was used which had a slight amount of calcite in it.

In the first attempt two cubic centimeters of dilute sulphuric acid were added to one gram of raw coal in the crucible and the crucible was set over a flame turned very low until the evolution of white fumes ceased, showing that all the sulphuric acid was evaporated. The carbonaceous matter was all burned out and the crucible was ignited over a blast lamp for fifteen

minutes. This method was not satisfactory for considerable spattering occurred which occasioned a loss of coal, thus vitiating the results. There is also the probable reduction of CaSO_4 in the presence of red hot carbon to CaS . To eliminate this source of error in the next experiment, the dilute sulphuric acid was not added until the carbonaceous matter was all burned out. The acid reacted readily with the ash and no spattering occurred when the liquid was subsequently evaporated. However, after ignition on the blast lamp the mass was found to be fused to the bottom of the crucible, making it impossible to detach it. Duplicates by this method checked very well as the following results show.

Coal No.	Ash, moistened with dilute H_2SO_4 .	
4787	5.53%	5.54%

These results are not sufficient in themselves to warrant any conclusions as to the value of this method but they warrant further work which is now being carried on in this connection by Professor Parr and Mr. J.M. Lindgren of the Illinois State Geological Survey Laboratory. The results so far obtained all indicate that this method can be developed into a very good one for ash determinations.

IX.- Qualitative Analysis of Ash.

The next proceeding was to analyze the ash qualitatively. The ash of coal 4993 was used. The first constituent looked for was sulphide. This was tested for in the same way as described on p.8 above. No traces of hydrogen sulphide were found, showing that no calcium sulphide was formed in the process of ashing.

A fresh quantity of the ash was next shaken up with water and warmed. The water extract was tested for alkalinity with red litmus paper. The red litmus paper was turned blue showing that there was alkali present. This basic reaction was due to calcium hydroxide, showing that calcium oxide, or free lime was present in the ash.

Some of the ash was then digested with dilute hydrochloric acid to dissolve any calcium sulphate present, and the hydrochloric acid extract was tested for sulphate by adding barium chloride solution to it. A white precipitate indicated barium sulphate. This showed that calcium sulphate was present in the ash of the coal.

The source of this sulphate was now to be sought. It was to be determined whether sulphates exist in the raw coal or are formed in the process of burning. The raw coal was digested for two hours at boiling temperature with a ten per cent solution of hydrochloric acid. The coal was filtered off, washed with hot water and the filtrate was tested for sulphate with barium chloride solution, just as in the case of the ash. Sulphate was found in the raw coal.

X.- Ash Determined in Milk Dishes.

The fact that sulphate was present in both the raw coal and the ash lead to a search for some possible connection between the two. The ash, as heretofore determined in porcelain crucibles, could not be used, for it was sintered to the crucibles and could not be removed. Even when the ash was scraped out with a spatula some chips of porcelain were always present. In seeking to eliminate these effects the ash was

determined in shallow flat bottomed dishes such as are used in milk analysis to determine total solids and ash in milk. The dishes were about seven centimeters in diameter by about one centimeter deep.

A one gram sample of coal was used for the determination, and was spread over the bottom of the weighed dish. By spreading out the coal in this fashion a large surface was exposed to the air and the carbonaceous matter was burned out more quickly and completely than in the case of the crucible determination. The gaseous products of combustion were readily carried off into the air. After the carbonaceous matter had been burned out over a free flame from a Tunsen burner turned very low, the white or nearly white ash was ignited for ten minutes in a muffle heated to nine hundred degrees C. to nine hundred and fifty degrees C. to decompose any carbonate remaining in the ash. The ash was ignited to a very fine white powder and was not sintered at all to the dish, but could be brushed out completely. This method gave an ash which could be readily used for analysis so it was used in all subsequent ash determinations.

The work on the artificial samples of coal mixed with varying percentages of calcium carbonate was repeated, using the above described method. The amounts of coal and calcium carbonate were weighed separately and mixed in the dish. The mixture was spread out uniformly over the bottom of the dish and the carbonaceous matter was burned out over a low flame. The dish and contents were then ignited for ten minutes in a muffle to eliminate any chance that the calcite might take up

sulphur in the form of sulphur dioxide or sulphur trioxide from the flame.

For this work coal number 4993 was again used, since it contained no calcite. Samples were made up as before, containing respectively two, four, six, eight, and ten per cent calcium carbonate, the coal and calcium carbonate being weighed out separately for each one and mixed in the dish. The ash of the coal was determined and a series of values was also calculated by adding the percentage of ash in the coal taken to the calcium oxide resulting from the decomposition of the calcium carbonate used. The following table shows how the calculated results compared with the results actually obtained.

Table No. 7.

Lab. No. and Description of sample	Calculated Ash.	Ash actually obtained.
4993		8.50
4993 2% CaCO_3	9.51	9.66
4993 4% CaCO_3	10.46	10.60
4993 6% CaCO_3	11.41	11.57
4993 8% CaCO_3	12.36	12.58
4993 10% CaCO_3	13.30	13.57

The results actually obtained were in every case higher than the calculated values. This indicated that some compound of greater molecular weight than calcium oxide was formed during the process of ashing.

XI.- Quantitative Analysis of Ash.

To verify the above assumption the ash was analyzed. Qualitative tests for sulphide using the alkaline lead nitrate

method given on page 24 failed to disclose the presence of even traces of this constituent. Sulphate, present as calcium sulphate in the ash was then considered to be the disturbing factor in the ash. To determine this quantitatively the ash, obtained from a new sample, was boiled with one hundred cubic centimeters of a ten per cent hydrochloric acid solution in a three hundred cubic centimeter Jena beaker for about one hour. The solution was then filtered into a one hundred cubic centimeter volumetric flask and the solution, when cool, was diluted to the mark. Twenty-five cubic centimeters were taken for analysis so that the results obtained had only to be multiplied by four to get the total amounts in the ash.

The sulphur was determined in one of the twenty-five cubic centimeter fractions by diluting the liquid to about one hundred cubic centimeters and heating to boiling. The sulphate was then precipitated out by adding ten cubic centimeters of a ten per cent solution of barium chloride and continuing the boiling until all the barium sulphate was precipitated, and settled to the bottom. The barium sulphate was then allowed to stand for one hour to completely settle, and was then filtered out. The precipitate on the filter paper was washed six times with hot water to insure complete removal of impurities. The filter paper and contents were then ignited in a weighed porcelain crucible. The ignition was started at a very low heat to dry the paper, and then the temperature was raised to char it. When the paper was all "smoked off" the crucible was raised to a red heat to burn out all carbonaceous material and

was finally blasted for ten minutes to insure the complete removal of carbon and water which clings very tenaciously to a precipitate of barium sulphate. The crucible was then cooled in a desiccator and weighed.

The iron and calcium were determined volumetrically in one sample. Twenty-five cubic centimeters of the solution were diluted to about fifty cubic centimeters and were heated to boiling. Two or three drops of concentrated nitric acid were added to oxidize and ferrous salts that were present to ferric, and the iron and aluminum were precipitated out with ammonium hydroxide. The liquid in the beaker was boiled to coagulate and settle the precipitated hydroxides. The precipitate was filtered off and washed four times with hot water, the washings being allowed to run into the filtrate. The filtrate was set aside for the calcium determination. The iron and aluminum hydroxides were dissolved in dilute hydrochloric acid, boiled, and the iron was reduced with five drops of stannous chloride solution added while the solution was boiling. The solution was then diluted to about three hundred cubic centimeters, cooled, and ten cubic centimeters of a saturated solution of mercuric chloride were added to oxidize any excess stannous chloride in the solution. The solution was then titrated with a standard solution of potassium permanganate to determine the iron present.

The filtrate from the iron and aluminum hydroxides was made alkaline with ammonia and was heated to boiling. Ten cubic centimeters of a boiling saturated solution of ammonium

oxalate were added to the hot solution to precipitate the calcium and the liquid was boiled to cause the calcium oxalate to settle. The precipitated calcium oxalate was filtered off, and thoroughly washed several times with water, rinsing out the beaker onto the filter paper the first few times. The filter paper was then spread against the side of the beaker in which the precipitation took place, and the precipitate was washed off the paper into the beaker, the last two washings being with ten per cent sulphuric acid. Fifty cubic centimeters of water and ten cubic centimeters of concentrated sulphuric acid were then added to dissolve the precipitate. The solution was boiled and was titrated with standard potassium permanganate solution to determine the calcium according to the method used by Meade (8) for the determination of lime in Portland cement and raw materials used in cement manufacture.

The following table shows the results obtained in this analysis.

Table No. 2.				
Analysis of Ash, Referred to Original Coal.				
Description of Sample	Fe	CaO	SO ₃	CaSO ₄ equivalent to SO ₃
4993	1.067	.767	.317	.867
4993 2% CaCO ₃	2.96	1.80	.37	1.11
4993 4% CaCO ₃	2.90	2.90	.70	1.19
4993 6% CaCO ₃	2.83	4.00	.80	1.11
4993 8% CaCO ₃	2.74	5.10	.86	1.12
4993 10% CaCO ₃	2.67	6.20	.86	1.12

The surprising uniformity of results shown in the fourth column, headed SO_3 , lead to the conclusion that the calcium carbonate which had been added was in some way responsible for the retention of the sulphate in the ash. This was further borne out by the fact that the sulphate was lower in the ash of the raw coal alone, which contained no calcium carbonate.

To verify this assumption the raw coal was analysed. one gram of the coal was digested with ten per cent hydrochloric acid for one hour, filtered, washed, and the filtrate was made up to one hundred cubic centimeters just as in the case of the ash, as previously described. Twenty-five cubic centimeters of the solution were taken for analysis. The iron was precipitated out with ammonia and titrated with permanganate solution as above described. The sulphate was precipitated out with barium chloride solution and weighed. The iron and sulphate were both calculated to ferrous sulphate. The results checked each other showing that the sulphate was present as ferrous sulphate. Table No. 9 shows the results obtained.

Table No. 9.

Calculation of Sulphate to FeSO_4 from SO_3 and Fe Determinations.

.0208 g. FeSO_4 are equivalent to .0135 g. FeSO_4

.00499 g. Fe are equivalent to .0133 g. FeSO_4

The ferrous sulphate was calculated to calcium sulphate in which combination it would be most likely to appear in the ash. The .0134 grams of ferrous sulphate is equivalent to .0119 grams of calcium sulphate. This amount of calcium sulphate is the greatest amount that would appear in the ash if all the sulphur

trioxide from the ferrous sulphate were retained by the calcium oxide in the ash. A new series of values for the ash was calculated. The ash of the coal itself contained eighty-six hundredths of one per cent calcium sulphate or .0086 grams. In making the calculations the proper proportion of this .0086 g. CaSO_4 had to be allowed for in the ash. The difference between this amount of CaSO_4 , and the total amount possible to form on the above assumption that all the sulphate appeared as calcium sulphate in the ash, was considered to be formed by the excess SO_3 and the required amount of CaO coming from the decomposition of the calcium carbonate added. The balance of the lime added was figured in simply as calcium oxide. The ash obtained from the proportionate amount of coal taken was used as such in the calculations. To recapitulate, the calculated ash consists of three factors; first the ash of the coal itself including the calcium sulphate found in the ash; second, the calcium sulphate formed from the lime added and the excess sulphate found in the raw coal above that present in the ash; third the balance of the calcium oxide resulting from the decomposition of the calcium carbonate added, above that required for the formation of calcium sulphate.

The following calculations show the method by which the value of the calculated ash for the mixture containing ninety-eight per cent coal and two per cent CaCO_3 was obtained

$$(1) \quad .0086 \times .98 = .00839 \text{ g. ash in 98\% coal}$$

$$(2) \quad .0196 \times 136/200 = .01148 \text{ g CaSO}_4 \text{ equivalent to BaSO}_4 \text{ weighed.}$$

- (3) $.0086 \times .98 = .0084$ g CaSO_4 in 98% of ash
 CaSO_4 in ash
- (4) $.0113 - .0084 = .0031$ g CaSO_4 formed from excess
 CaO and SO_3
 of mixture.
- (5) $.0031 \times 55/136 = .0013$ g CaO equivalent to
 CaSO_4 in (4)
- (6) $.0112 - .0013 = .0099$ g CaO excess
 CaO in CaCO_3
 added.

Thus the calculated ash of 98% coal and 2% CaCO_3 consisted of

Ash from 98% coal	8.39
CaSO_4 formed above that present in the ash	.31
CaO above that required to combine with SO_3	.49
total	9.19
Ash as determined	9.19

The values for the ash of the other mixtures were calculated exactly as above outlined.

The ash of these mixtures was determined by weighing out the proper proportions of coal and calcium carbonate into the dishes and mixing them in the dish. The mixture was then spread uniformly over the bottom of the dish and the dish was placed over a bunsen burner. It was heated at a low temperature until all the carbonaceous matter was burned out and was then placed for fifteen minutes in a muffle heated to about 700° C. to ignite it and to decompose the calcium carbonate. The dishes were then cooled in a desiccator and weighed.

Table number ten shows the results as obtained and also gives the calculated values for the ash.

Table No. 10
Comparison of Ash in Coal 4993.

Description of Sample	Calculated ash.	Ash as obtained.
4993		8.56
98% 4993 2% CaCO_3	9.25	9.66
96% 4993 4% CaCO_3	10.63	10.66
94% 4993 6% CaCO_3	11.59	11.57
92% 4993 8% CaCO_3	12.56	12.61
90% 4993 10% CaCO_3	13.51	13.57

The agreement of the actual ash values obtained with the calculated values is very close showing that the ash is formed as indicated by the theory on which the calculations were made. It also shows that the calcium carbonate on decomposing to calcium oxide and carbon dioxide takes up sulphur trioxide and forms calcium sulphate.

Table number eleven shows the distribution of sulphate in the raw coal and the ash. The sulphate in the raw coal is given as calcium sulphate to facilitate comparison with the calcium sulphate in the ash.

Table No. 11.
Distribution of Sulphate in Coal 4993.

Description of sample.	CaSO_4 in ash of coal.	CaSO_4 formed from excess CaO	CaSO_4 in ash of mixtures.	CaSO_4 equivalent in raw coal
4993	.86%			1.19%
98% 4993 2% CaCO_3	.84	.31	1.15%	1.17
96% 4993 4% CaCO_3	.83	.36	1.19	1.14
94% 4993 6% CaCO_3	.81	.31	1.12	1.12
92% 4993 8% CaCO_3	.79	.33	1.12	1.09

90% 4993	10% CaCO_3	.77	.35	1.12	1.07
----------	---------------------	-----	-----	------	------

The close agreement of the calcium sulphate found in the ash of the mixtures with that found in the raw coal indicates that the calcium carbonate has the effect of retaining the sulphate in the raw coal as calcium sulphate in the ash.

The next coal taken up was number 5123. This was analyzed just as in the case of number 4993. The ash was determined in shallow dishes and mixtures carrying two, four, six, and eight per cent of calcium carbonate were made up. The theoretical value for the ash of these mixtures was calculated just as shown for coal number 4993, and the ash was determined and analyzed for sulphate.

The results for sulphate given below are stated in terms of calcium sulphate since that is the way it would be combined in the ash. The value of the ash was nine and seventy-four hundredths per cent. The sulphate in the raw coal was equivalent to fifty-one hundredths of one per cent calcium sulphate. The coal was analyzed for calcium and an equivalent of twenty-two hundredths of one per cent calcium sulphate or sixteen hundredths of one per cent calcite was found. The ash of the coal contained twenty-one hundredths of one per cent calcium sulphate.

Table No. 12 shows how the calculated results compared with the results obtained.

Table No. 12.

Comparison of Ash Values in Coal 5123.

Description of Sample		Theoretical ash as calculated.	Actual ash value as obtained
5123			9.74%
98% 5123	2% CaCO_3	10.85%	10.87
96% 5123	4% CaCO_3	11.76	11.94
94% 5123	6% CaCO_3	12.71	12.78
92% 5123	8% CaCO_3	13.65	13.72

This table shows the same agreement between the calculated values and those actually obtained by burning the coal that is evident in the case of coal number 4903. The excess sulphate is evidently all retained by the calcium carbonate added.

Table number thirteen shows the distribution of sulphate in this coal.

Table No. 13.

Distribution of Sulphate in Coal 5123.

Description of sample.		CaSO_4 in ash of coal.	CaSO_4 formed from excess CaO	CaSO_4 in ash of mine lumps.	CaSO_4 equiv- alent in raw coal.
5123		.22%			.51
98% 5123	2% CaCO_3	.22	.29%	.51	.51
96% 5123	4% CaCO_3	.21	.28	.49	.50
94% 5123	6% CaCO_3	.21	.33	.54	.48
92% 5123	8% CaCO_3	.20	.36	.56	.47

The results in this table also show that the calcium

carbonate is effective in retaining the sulphate in the ash that is present in the raw coal.

To test these facts farther seventeen other coals were selected and analyzed in the same way as those just discussed. These coals all had sufficient calcite present as shown by the carbon dioxide determination, not to make necessary any addition of calcium carbonate. The ash was determined by the same method as the preceding. Table number fourteen shows the disposition of the sulphate in these samples. The results are given in terms of sulphur trioxide and referred to the original coal calculated to the dry basis.

Table No. 14.

Lab. No.	Disposition of Sulphate.			
	CaO calculated from CO ₂	SO ₃ in raw coal.	SO ₃ found in ash.	SO ₃ lost or gained in ash.
5365	1.10	.95	.94	-.01
5367	1.02	.39	.38	-.01
5370	1.46	.47	.48	+ .01
5372	.45	.67	.62	-.05
5376	.36	.61	.59	-.02
5382	1.12	1.42	1.40	-.02
5391	.43	.62	.60	-.02
6303	1.83			
6304	.36	.31	.31	.00
6305	.50	.26	.26	.00
6306	2.15	.21	.21	.00
6307	2.70	.27	.27	.00
6308	1.44	.20	.20	.00
6309	1.37	.23	.22	-.01

6310	.95	.21	.22	+.01
6311	.53	.27	.27	.00
6312	1.35	.13	.13	.00

This table shows the same agreement between the sulphate present in the raw coal and the found in the ash that is evident from the study of coals number 4093 and 5153.

The ash of each of the samples given in the above table (No. 14) was obtained by burning off the carbonaceous matter and pyritic sulphur at a very low temperature so that there was no dissociation of calcium carbonate. The vapor pressure of calcium carbonate at six hundred degrees C. is about eighty mm. of mercury (30) while at seven hundred degrees it is about two hundred mm. showing that at the lower temperature there is practically no calcium oxide formed, and that at the latter temperature there is considerable free lime present even though the dissociation temperature of calcium carbonate is nine hundred degrees C. This explains why there is a much greater amount of calcium sulphate present in the ash of a coal which has been burned off at a cherry red heat (about seven hundred degrees C.) when there is still pyritic sulphur present to combine with the calcium oxide than there is present in the ash of the same coal burned off at a temperature not higher than six hundred degrees C. Table Number Fifteen shows the effects of slow burning at a low temperature and quick burning at a high temperature.

Table No. 15.		
Effects of Rate of Combustion.		
Coal No.	Sulphate in Ash.	
	Low Temp.	High Temp.
6306	.215	.20
6307	.27	.22

Conclusions.

1. Carbonates such as calcite, sulphates, as ferrous or ferric sulphates and sulphides or iron pyrites are present in coal. They occur with sufficient frequency and in amounts generally great enough to make their estimation necessary in seeking a value for the true ash of coal.

2. Calcium carbonate decomposes into calcium oxide and carbon dioxide, with loss of the CO_2 . Calcium oxide will take up sulphur from the coal or from the flame and retain it as calcium sulphate in the ash after ignition. If the carbonaceous matter and pyritic sulphur are burned out of the coal at a temperature below six hundred degrees that is at a temperature below the point of decomposition of CaCO_3 and thus at a point not favorable for the formation of CaO the only sulphate present in the ash will be that present as ferrous sulphate in the raw coal. The reason for this is that calcium carbonate is not decomposed at six hundred degrees. However, if the coal is ashed at seven hundred degrees the calcite is very appreciably decomposed and thus may take on pyritic sulphur in addition to the sulphate sulphur.

Sulphates are present in the raw coal as ferrous and ferric sulphates. Ferrous sulphate decomposes at about six

hundred degrees and ferric sulphate at about seven hundred degrees into sulphur trioxide, sulphur dioxide, free oxygen and ferric oxide.

Sulphide present as iron pyrites turns to sulphur dioxide and ferric oxide although under certain conditions it oxidizes to ferrous or ferric sulphate in the raw coal.

3. The coal should be ashed in a muffle furnace using a shallow flat dish with good circulation of air instead of a crucible in order to insure removal of carbon dioxide. The temperature should be lower than six hundred degrees until all the carbonaceous matter and free sulphur are burned out. When that is completed the temperature should be raised to nine hundred to nine hundred and fifty degrees to insure decomposition of the calcium carbonate.

4. From a consideration of the above description it will be seen that the ash as weighed contains the calcium carbonate as calcium oxide and the ferrous and ferric sulphates as ferric oxide. To correct the ash the carbon dioxide equivalent to the calcium carbonate should be added to the ash as weighed and the sulphur trioxide found in the raw coal as FeSO_4 should be added to the iron present in the ash as Fe_2O_3 . That is to say $1/2 \text{ O}$ has been added by oxidation of FeO hence the SO_3 should be decreased by that amount before adding the correction for SO_3 .

5. If it is desired to ash the coal at temperatures around seven hundred degrees it must be remembered that the calcium carbonate has been appreciably decomposed and has taken on all the sulphate sulphur present in the raw coal in addition

to an indefinite amount of pyritic sulphur. Hence in working at this higher temperature it is best to convert all the calcium oxide to calcium sulphate by moistening the ash with sulphuric acid and then correcting for the excess sulphate added. This excess would be equivalent to 9/11 of the CO_2 present in the raw coal that is

$$\begin{array}{rcl} \text{SO}_3 & = & 80 \\ 9/11 \text{ of } \text{CO}_2 & = & 36 \\ \text{or } 44 & & \underline{\quad} \end{array}$$

Difference $44 =$ equivalent of CO_2 .

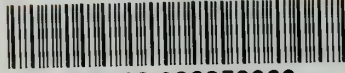
References

1. U. of I. Engineering Experiment Station, Bulletin No. 37.
2. Original Communications, 8th. International Congress of Applied Chemistry, Vol. 10, p. 215.
3. Illinois State Geological Survey, Bulletin No. 16.
4. U. of I. Engineering Experiment Station, Bulletin No. 46.
5. U. of I. Engineering Experiment Station, Bulletin No. 46.
6. Journal of the American Chemical Society, 26, 294, (1904)
The diagram of this apparatus is shown in U. of I. Engineering Experiment Station, Bulletin No. 37, p. 23.
7. Journal of the American Chemical Society, 31, 237, (1909).
8. Portland Cement, R. K. Meade, p. 174.
9. Journal of the American Chemical Society, Vol. 31, p. 1116.
10. Geological Survey of Ohio, Bulletin No. 9, p. 316.
11. S. W. Parr, The Chemical Examination of Water, Fuel, Flue Gases and Lubricants, p. 73, (1911).
12. Chemiker Zeitung, XXXVI, 80, p. 757, (July 4, 1912.)
13. U. of I. Engineering Experiment Station, Bulletin No. 37.
14. U. of I. Engineering Experiment Station, Bulletin No. 46, p 37.
15. Ladenburg, Handwörterbuch der Chemie, III, p. 520.
Dammer, Handbuch der Anorganischen Chemie, III, p. 329.
16. U. of I. Engineering Experiment Station, Bulletin No. 37, p 25
17. Chemiker Zeitung, XXXVI, 80, p. 757, (July 4, 1912).
18. U. of I. Engineering Experiment Station, Bulletin No. 46, p.42.
19. Treadwell-Hall, Analytical Chemistry, Second Edition, (1911)., I, p. 292.
20. Le Chatalier.





UNIVERSITY OF ILLINOIS-URBANA



3 0112 086859060